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14. ABSTRACT
Funds from a DURIP equipment grant were used to augment the ultrafast IR 2D vibrational echo spectrometer. The major improvement involved a new dual MCT array detector composed of two 32 x 1 element MCT IR detector arrays. The dual array makes it possible to improve signal-to-noise ratio in the heterodyne detection of the vibrational echo signal. To implement the revamping of the system, new optics to implement the two beam geometry were put in place and precision translation stages required to control the path lengths to fractions of a wavelength of light obtained. The instrument has been used make the first measurements of ultrafast chemical exchange, making in possible to study fast solute solvent complex dynamics and isomerization in room temperature solutions under thermal equilibrium conditions.

15. SUBJECT TERMS
vibrational echo; correlation spectroscopy; ultrafast infrared; dynamics of molecules; hydrogen bond dynamics; complexes, isomerization infrared spectroscopy; density dependence

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Enhanced Vibrational Echo Correlation Spectrometer for the Study of Molecular Dynamics, Structure, and Analytical Applications

This DURIP grant provided funds to make substantial changes in the existing ultrafast 2D IR vibrational echo spectrometer. The nature of the experiment and the modifications made using the equipment funds are briefly outlined.

In a 2D IR vibrational echo experiment, three ultrashort IR pulses tuned to the frequency of the vibrational modes of interest are crossed in the sample. Because the pulses are very short, they have a broad bandwidth, which makes it possible to simultaneously excite a number of vibrational modes or a very broad spectral feature such as the hydroxyl stretch band of water. The times between pulses 1 and 2 and pulses 2 and 3 are called τ and T_w, respectively. At a time $\leq \tau$ after the third pulse, a fourth IR pulse is emitted in a unique direction. This is the vibrational echo, the signal in the experiments. A qualitative description is given of how the vibrational echo pulse arises and how it is possible to obtain phase information, not just the intensity, from the vibrational echo.

The first pulse in the sequence places the vibrational oscillators into a coherent superposition state of the vibrational ground state (0) and vibrational first excited state (1), with all of the oscillators initially oscillating in phase. The initial macroscopic phase relationships among the oscillators decay rapidly. This is called the free induction decay. The phase relationships can decay for a number of reasons. Several peaks in the IR spectrum may be excited. These are at different frequencies, so the vibrational oscillators oscillate at different intrinsic frequency. Even for a single mode, molecules in different environments, e.g., different local solvent structures, will have different oscillator frequencies, which is called inhomogeneous broadening. In addition, there are dynamic interactions with the environment, e.g., local solvent structure fluctuations, which cause the frequency of a given oscillator to evolve in time. These frequency fluctuations are called dynamic dephasing and spectral diffusion. The rest of the pulse sequence can preserve information about the phase relationships that are seemingly lost during the free induction decay. Only the spectral diffusion at sufficiently long time can totally destroy the phase relations among the oscillators that cannot be recovered by the rest of the pulse sequence. However, even then, the signal is not zero because the initial two pulses also set up a spatial relationship among the oscillators that contributes to the signal.

The second pulse in the sequence stores the phase (and spatial) information induced by the first pulse as a complex frequency and spatial pattern of differences of the populations of the 0 and 1 vibrational states. After the waiting period, T_w, the third pulse again generates coherent superposition states of the oscillators. Initially, the oscillators are not in phase, but the pulse sequence initiates a rephasing process. At a time $\leq \tau$ after the third pulse, the vibrational oscillators are again oscillating in phase. Each vibrational oscillator has associated with it a microscopic oscillating electric dipole. When rephasing has occurred and all of the oscillators are in phase, the sample has a macroscopic oscillating electric dipole. A macroscopic oscillating electric dipole emits radiation, which is the source of the vibrational echo. The vibrational echo pulse is short because the oscillators again get out of phase just as they did after the first pulse.

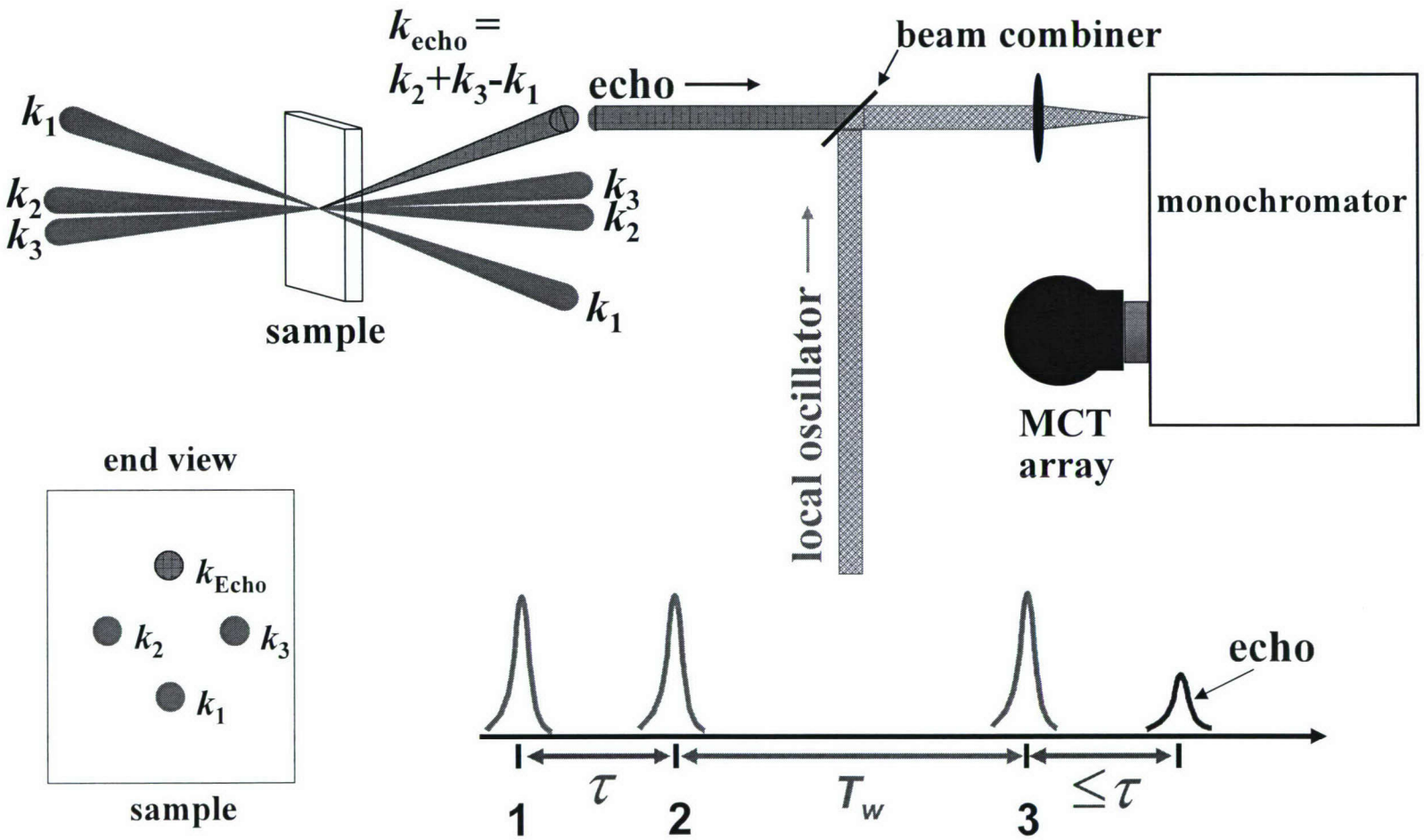
Both the intensity of the 2D vibrational echo pulse and its time structure contain important information. If the echo pulse is sent directly into an IR detector, its intensity is measured, but phase information is lost. Phase information is obtained by allowing the vibrational echo pulse to interfere with another pulse, called the local oscillator. Interference can provide phase information just as in a spatial interference pattern created by two crossed laser beams. In a spatial interference pattern, the fringe pattern is observed as a spatial variation in the intensity, which gives information on the phase relations of the electric fields of the two beams. In the heterodyne detected vibrational echo experiments, the local oscillator pulse and the vibrational echo pulse are collinear, and the phase information is obtained by observing the interference pattern (interferogram) as a function of time.

In a dynamic system, the first laser pulse "labels" the initial structures of the species in the sample. The second pulse ends the first time period τ and starts clocking the "reaction time," during which the "labeled" species experience population dynamics. The third pulse ends the population dynamics period of length T_w, and begins a third period of length $\leq \tau$, which ends with the emission of the echo pulse. The echo signal reads out the information about the final structures of all labeled species. There are two types of time periods in the experiment. The periods between the pulses 1 and 2 and between pulse 3 and the echo pulse are called

coherence periods. During these periods the vibrations are in coherent superpositions of two vibrational states. Fast vibrational oscillator frequency fluctuations induced by fast structural fluctuation of the system cause dynamic dephasing, which is one contribution to the line shapes in the 2D spectrum. During the period T_w between pulses 2 and 3, called the population period, a vibration is in a particular state not a superposition state. Slower structural fluctuations of the system, spectral diffusion, contribute to the 2D line shapes. Other processes during the population period also produce changes in the 2D spectrum. For example, chemical exchange can occur in which two species in equilibrium are interconverting one to the other without changing the overall number of either species. Chemical exchange causes new peaks to grow in as T_w is increased. In an experiment, τ is scanned for fixed T_w. The recorded signals are converted into a 2D vibrational echo spectrum. Then T_w is increased and another spectrum is obtained. The series of spectra taken as a function of T_w provides information on dephasing, spectral diffusion, and population dynamics.

A 2D IR vibrational echo experimental setup is illustrated schematically in the figure. Briefly, three successive ultrashort IR pulses with wave vectors (propagation directions) k_1, k_2, and k_3 are applied to the sample to induce the subsequent emission of the time delayed vibrational echo, in a distinct direction ($k_e = -k_1 + k_2 + k_3$). The IR pulses (~50 fs) are produced using a regeneratively amplified Ti:Sapphire laser pumped optical parametric amplifier system. The vibrational echo pulse is detected with frequency and phase resolution by interfering it with a 5th (local oscillator) pulse, and the combined pulses are dispersed in a monochromator and then detected with the new 2x32-element MCT IR array detector. As discussed above, the function of the local oscillator is to phase resolve (through the interferogram between the echo and local oscillator) and optically heterodyne amplify the vibrational echo signal.

The major component purchase with this DURIP grant is the dual 32 element MCT IR array detector. To perform the experiment, many frequencies must be detected. The array makes it possible to detect 32 wavelengths at once, reducing experiments that would take a month to experiments that take a day. The dual array provides a tremendous advantage over a single 32 element array by permitting shot-to-shot normalization of the signal. Two beams are directed into the monochromator. One is the combined vibrational echo/local oscillator. The other is an equal amplitude piece of the local oscillator. (The two beams entering the monochromator are not shown in the figure.) The two beams are displaced vertically. At the array, the signal/local oscillator beam hits the top stripe of 32 MCT elements, and the local oscillator beam alone hits the bottom stripe. On each laser shot at 1 kHz rep rate, both trips are read out and processed. The 32 intensities on the bottom stripe are used to normalize out shot-to-shot fluctuations in laser intensity at each of the 32 wavelengths. The result is a tremendous improvement in the signal-to-noise ratio. The other funds in the equipment grant were used to implement the new dual array system. In particular optics, optical mounts, and precision translation stages were obtained.


k_{echo} =
k_2+k_3-k_1
echo
beam combiner
k_1
k_2
k_3
k_3
k_2
k_1
sample
local oscillator
monochromator
MCT
array
end view
k_{Echo}
k_2
k_3
k_1
sample
echo
τ
T_w
$\leq\tau$
1
2
3